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Analysis of single and binary phases in cerium doped sodium bismuth titanate -$Na_{0.5}Bi_{0.5}TiO_3$ materials

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Abstract

The pure and cerium doped sodium bismuth titanate inorganic powders were synthesized by solid state reaction method. The presence of rhombohedral phase was observed in cerium doped NBT compounds. At 1200 ºC, the 5% of cerium doped NBT compound forms single perovskite phase. The samples of x = 0.10 and 0.15 were heat treated to 1350 ºC, the binary phases with cerium and bismuth oxides were observed. The X-ray diffraction, fourier transform infrared spectroscopy, reflectance spectra, differential thermal analysis and thermo gravimetric analysis were used to analyze the various properties of samples. Moreover, the effects of cerium doping and calcining temperature on NBT samples were investigated. In this work we present our recent results on the synthesis and characterization of Ce doped sodium bismuth titanate materials.

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Keywords: Electroceramics; inorganic; XRD; FT-IR; thermal analysis.

1. Introduction

Piezoelectric and ferroelectric materials are used in wide range of applications such as accelerators, transducers, filters and resonators, actuators, microelectromechanical systems (MEMS) and random access memories (RAM). The lead (Pb) containing compounds like lead titanate and lead zirconate titanate (PZT), are restricted for use in consumer products due to its high toxicity[1].

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It became necessary to use environmental friendly materials nowadays. $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) pure sample is well known as an excellent key material for the superior ferroelectric and piezoelectric properties. The phase transition temperature for NBT compounds is from 320 ºC to 800 ºC [2]. Comparing with other lead free ceramic materials the NBT reveals good piezoelectric properties and large remnant polarization with strong ferroelectric properties. It is very difficult to pole the pure NBT due to its lower coercive field. In recent years, the extensive studies proved that it is easy to pole A-site substituted NBT compounds [3, 4]. Based on this we focused the substitution of cerium on NBT compounds.

The phase transition between the rhombohedral and tetragonal ferroelectric phases can be termed as 'morphotropic phase boundaries'. The perovskite type solid solution with MPB region shows excellent properties such as dielectric, piezoelectric and ferroelectrics. Because of large dielectric and piezoelectric constants these MPB materials plays important role in sensors and electrostrictive actuators [5]. Considering that NBT ceramics have perovskite phase, we investigated the cerium doped NBT as single and binary phase materials. Moreover, special emphasis was focused on searching for the perovskite single phase system to achieve great enhancement in the thermal, optical and electrical properties. With various cerium composition ranges, the NBT compound was analyzed through XRD. In the present work, the $Na_{0.5}Bi_{(0.5-x)}Ce_xTiO_3$ (x = 0.05 to 0.15) (NBCT) solid solutions were prepared by the solid state reaction method and their structural, optical and thermal properties were analyzed systematically.

2. Experimental procedure

The pure and cerium (Ce) doped sodium bismuth tianate-$Na_{0.5}Bi_{(0.5-x)}$ Ce_xTiO_3 (NBCT) (x = 0.05, 0.10 and 0.15-NBCT-1, 2 and 3 respectively) ceramics were synthesized by solid state reaction method. The reagent grade of Bi_2O_3, Na_2CO_3, CeO_2, TiO_2 (99.99% purity) were mixed with ethanol and ground for 2 hours. To obtain the single perovskite phase, the pure and cerium doped NBT samples were heat treated from 1200 to 1350ºC for 8 hours. The X-ray powder measurements were collected in a D5000 diffractometer with Cu-Kα radiation. FT-Infrared spectra were collected by FTIR spectrometer-Perkin Elmer-Spectrum GX-FTIR. The differential thermal analysis (DTA) and differential scanning caloriemetry (DSC) were performed at high temperature with a heating rate of 20 ºC/min with simultaneous thermal analyzer-SDT-Q600. The optical diffuse reflectance spectrum was obtained from reflectance spectrophotometer-Perkin Elmer-model no. Lambda-900.

3. Results and Discussion

3.1 Powder X-ray diffraction

Fig. 1 shows the powder X-ray diffraction pattern of pure and cerium doped sodium bismuth titanate samples. At 1200 ºC, the NBT and NBCT-1 form the single pervoskite phase. The cerium does not enter at the concentration range of x = 0.10 and 0.15. The peak splitting with super lattice reflections takes place at 2θ = 46 and 57.8º for NBCT-2 and 3 samples. These super lattice reflections confirms formation of binary phase [6]. The peak splitting at (200), (211) and (220) reflections for $x = 0.10$ and 0.15 nominal compositions confirms the formation of cerium and bismuth oxide binary phases [7, 8]. It is worth comparing the obtained data with previous literature results. The X-ray diffraction patterns give the evidence for NBT and NBCT-1 with rhombohedral structure. The appearance of peak splitting with super lattice reflection confirms the formation of the tetragonal structure in NBCT-2 and 3 samples [9]. The higher cerium content samples require high calcination temperatures to obtain a single phase. Except NBCT-2 and 3 samples all other samples transform to the single perovskite phase at 1200 ºC. In case of NBCT-2 and 3 samples, presence of small peak has been observed at 28 to 30.24 º (2θ). This small peak confirms the presence of small amount of cerianite-CeO_2 (JCPDS No: 33-0394) the binary bismuth oxide phase of $Bi_2O_{2.33}$, . data: 27-0051(JCPDS).

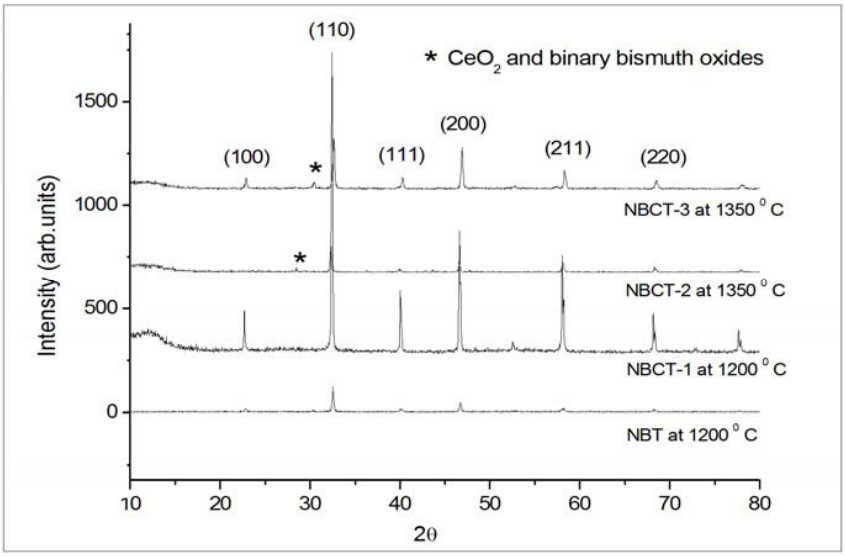

Fig. 1. X-ray diffraction of NBT and $Na_{0.5}Bi_{(0.5-x)}$ Ce_xTiO_3 powders.

It is not possible to further increase the calcination temperature of above 1350 ºC, due to the substantial loss of bismuth at elevated temperature that takes place in these samples. The temperature mentioned in the corresponding plot is the minimum and maximum temperature required for phase formation for all the pure cerium doped sodium bismuth titanate samples.

3.2 Rietveld refinement

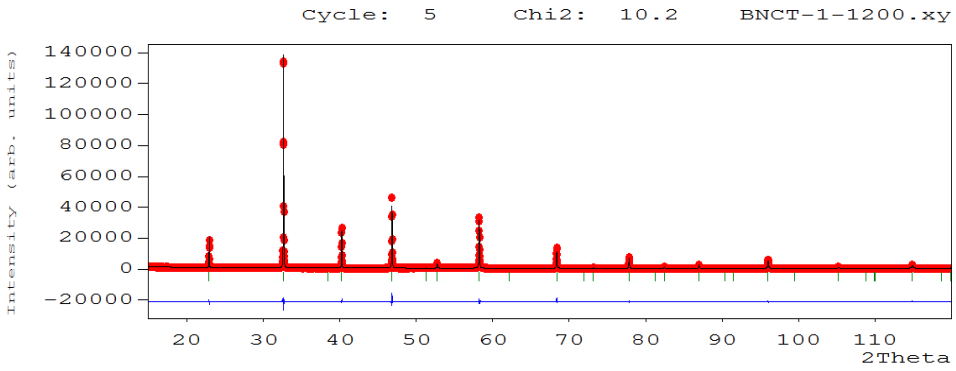

Fig. 2. Observed (■), calculated (red line), Bragg line (Green line) and difference (blue line) plot of refined data for NBCT-1 heat treated at1200 ºC .

Fig. 2 shows Observed (■), calculated (•), Bragg line (|) and difference (-) plot of refined data of NBCT-1 sample. The good fit between the observed and calculated profiles confirms that the structure of NBCT-1 is identical with pure NBT at 1200 ºC [10]. The lattice parameters are calculated as a=b=5.472 Å and c=6.770 Å. The obtained parameters are very close to the standard data of pure NBT (the Joint Committee of Powder Diffraction Standard (JCPDS) [11]. Due to the presence of binary phases, it is impossible to analyse the refinement data of other cerium

doped samples.

3.3 Functional group analysis-Fourier transform infrared spectroscopy (FT-IR)

The fourier transform infrared spectra of pure and cerium doped NBT powders were analyzed. Figure 3 represents the infrared spectrum of the as-synthesized NBT, NBCT-1, 2 and 3 powders. The stretching band from 669.22 to 1642.76 cm^{-1} indicates the presence of residual organic compounds in the synthesized powder. In addition, the formation of a titanate structure is confirmed with characteristic bands at 846.37 cm^{-1}. This band is attributed to Ti–O stretching vibrations. It can be noticed that as the content of cerium increases the intensity of absorption peaks from 1300 to 1700 cm^{-1} becomes weaker. Thus, the adsorption band at the range of 500–1700 cm^{-1} (669.22, 968.06, 1269.98, 1385.51, 1616.57 and 1642.76 cm^{-1}) completely changes the shape of the spectra [12].

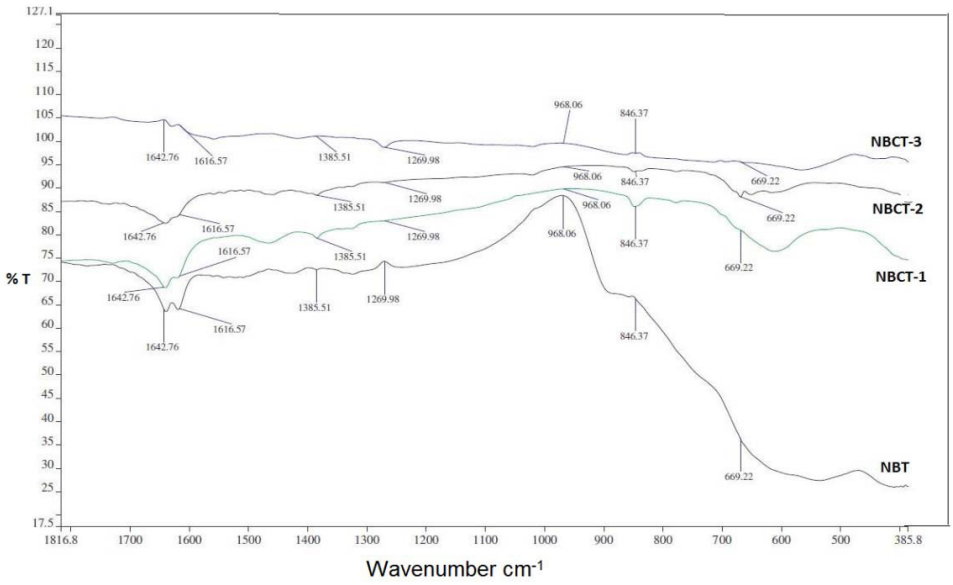

Fig. 3. The infrared spectrum of the NBT and NBCT powders.

The samples have an identical vibration model, with an asymmetric vibration band (within 500–1700 cm^{-1}). The stretching vibration of octahedral BO_6 groups can be observed in an asymmetric band in perovskite structure. This is due to change in the length of B–O bonds along c-axis [13-15]. In case of cerium doped samples, the small shift of the vibration band to lower wavenumber directions was observed. Moreover, it was noticed that the changes in the bands were observed due to doping by cerium. These changes are most probably due to significant differences in the rhombohedral to tetragonal structure as a result of the cerium addition.

3.4 Diffuse reflectance spectrum analysis

The diffuse reflection spectrum of NBT, NBCT-1, 2 and 3 samples were analysed**.** The ceramic powders heat treated at 1350ºC, were mixed and ground with KBr at a 1:20 ratio (i.e. 5% weight). The addition of KBr with these inorganic samples would lead to increase in the proportion of the infrared beam, which will reflected diffusely by the sample. The samples were pressed into cylindrical pellets of 10 mm in diameter with 1-2 mm thickness under hydraulic press at a pressure of 8 x 10^3 kg m^{-2}. The infrared radiation is focused on the surface of solid pellets.

The radiation is incident on the samples and emerges as reflectance spectrum. The data were collected from the infrared detector. The samples obtained from lower to higher cerium concentration exhibit significant changes in plot, which is comparable with the pure NBT sample[16]. The dramatic change in specular contribution to the spectral data has been observed according to concentration of cerium in NBT samples. The obtained data clearly indicates the homogeneity and the uniform fine particle sizes of the samples [17].

Particle size of doped samples can affect its colour and reflectance. According to the Kubelka–Munk (KM) theory, in general if the reflectance of a material increases, the particle size decreases. The reflectance of a sample depends upon the factors such as mean particle size, porosity, shape, surface texture, packing density, chemical composition like dopant material and wavelength. In case of NBT sample 71% of reflectance has been observed. In NBCT-1,2 and 3 samples, 52, 43 and 36% of reflectance has been observed respectively. The reflectance value is inversely proportional to concentration of cerium. Based on KM theory, difference in colour may be due to different ratio of cerium 3^+, 4^+ and different particle size [18].

3.5 Thermal analysis

The thermal behaviour of as milled NBCT-1, 2, 3 powders was analyzed by differential thermal analysis (DTA) and differential scanning caloriemetry (DSC). All the samples were heat treated up to 1300 ºC and then cooled to room temperature. Fig. 4(a), (b) and (c) illustrates the DTA and DSC results of all cerium doped NBT samples. The samples were heat treated and quenched in water. The figure shows the endothermic peak at 710.83, 724, 732.48 ºC for NBCT-1, 2 and 3 samples respectively. The endothermic peak value increases with respect to increase of cerium dopant. These peaks can be ascribed to the phase transformation of Bi_2O_3 from α phase to β phase [19, 20]. For NBCT-1 and 2 samples the two endothermic peaks were observed at 651.52 and 653.40 ºC. At this temperature range no endothermic peak has been observed in case of NBCT-3 sample. Instead of this, the strong endothermic peak has been observed at 627.05 ºC for this sample. The exothermic peaks were observed at the temperature range of 627.05, 628.93 and 660.93 ºC for NBCT-1, 2 and 3 samples respectively. The exothermic peak value decreases with respect to increase of cerium dopant. The appearance of these endothermic and exothermic peaks confirms the rhombohedral to tetragonal phase transition in cerium doped NBT samples [21]. There is no obvious endothermic or exothermic peak observed during weight loss of the samples.

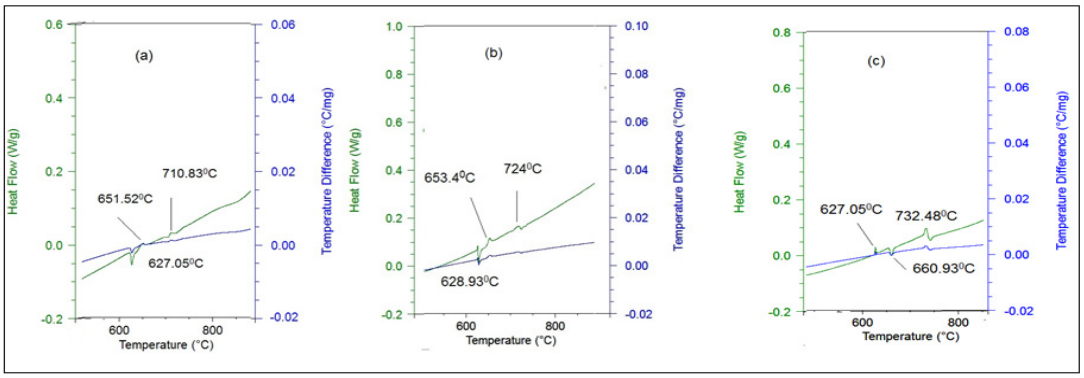

Fig. 4(a), (b) and (c). The thermal analysis curves for NBCT-1-(a), 2-(b) and 3-(c) samples.

4. Conclusion

The influence of different concentration of cerium in sodium bismuth titante powders at various temperatures was investigated. At 1200 ºC, the formation of perovskite phase has been observed for NBT and NBCT-1 samples. In case of NBCT-2 and 3 samples, the perovskite phase with minor secondary phase has been observed at 1350 ºC. The temperature range for the single and binary phase formation was increased depending on the amount of cerium content. The calcined sample with the highest amount of cerium exhibited the perovskite phase with binary bismuth oxide and cerianite phase. Moreover, the effects of cerium doping and calcining temperature on NBT samples were investigated. The cerium doped sodium bismuth titanate ceramics are expected to be a new and promising candidate for lead-free piezoelectric applications like micro-actuators and sensors. In addition, this work furthers the understanding the mechanism of calcining temperature ranges for the formation of the single perovskite structure.

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